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Request for grant of a patent

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01AUG02 E737677-1 D00239
P01/7700 0.00-0217794.7

1.	Your reference	JTS\P12318GB
2.	Patent application number *(The Patent Office will fill in this part)*	0217794.7
3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	The University Court of the University of St. Andrews College Gate North Street St. Andrews Fife, KY16 9AJ, Scotland, UK
	Patents ADP number *(if you know it)*	4049417004
	If the applicant is a corporate body, give the country/state of its incorporation	
4.	Title of the invention	Fuel Cell Electrodes
5.	Name of your agent *(if you have one)*	Cruikshank & Fairweather
	"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	19 Royal Exchange Square Glasgow, G1 3AE Scotland, UK
	Patents ADP number *(if you know it)*	547002

		Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*
6.	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number	-		

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7.	If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	-	

8.	Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* *a) any applicant named in part 3 is not an inventor, or* *b) there is an inventor who is not named as an applicant, or* *c) any named applicant is a corporate body.* *See note (d))*	Yes

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Continuation sheets of this form	
Description	9
Claim *(s)*	-
Abstract	-
Drawing *(s)*	4

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Priority documents	-
Translations of priority documents	-
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	-
Request for preliminary examination and search *(Patents Form 9/77)*	-
Request for substantive examination *(Patents Form 10/77)*	-
Any other documents *(please specify)*	-

11. I/We request the grant of a patent on the basis of this application.

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Date 31/072002

12. Name and daytime telephone number of person to contact in the United Kingdom: Mr Jan Szczuka - 0131 225 4500

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FUEL CELL ELECTRODES

The present invention relates to fuel cell electrodes, and more particularly to electrodes suitable for use in solid oxide fuel cells (SOFCs).

There is a great need for and interest in more efficient means of converting chemical energy into electrical energy, which has created great interest in fuel cells. The practical commercial development of these has, though, been held back by numerous practical problems. The SOFC is a particularly attractive system which can utilize hydrocarbon fuels such as methane with internal reforming of the fuel, and achieve relatively high efficiencies. Significant problems remain, though, in relation to inter alia the design of the anode used.

Many different materials have been tried in the search for improved anode performance, including materials such as Ni/ZrO_2 which has relatively good performance but suffers from the substantial disadvantage of relatively short working life due to the formation of carbon deposits when using hydrocarbon fuels, susceptibility to poisioning with sulphur which is frequently encountered in hydrocarbon fuels and an intolerance to repeated reduction/oxidation cycling, as was encountered in small systems such as CHP units or APUs for automotive applications. It has also been proposed to use $LaCrO_3$ (P. Vernoux et al J. Electrochem. Soc. 145 3487-3492 (1998)), and more recently it has been proposed to utilize $LaCrO_3$ which has been doped with various elements in order to improve its performance (J. Liu et al Electrochemical and Solid-State Letters 5 A122-A125 (2002)). Nevertheless even such doped $LaCrO_3$ has relatively limited electrochemical performance and effective working life.

It is an object of the present invention to avoid or minimize one or more of the abovementioned disadvantages.

It has now, by consideration of a novel approach, been found that by using a double perovskite material based on $LaCrO_3$ instead of a doped $LaCrO_3$, it is possible to achieve electrical and catalytic properties comparable with prior art anode materials such as Ni based anodes (that is with over-potential losses which can be less than 100 mV at current densities of 400 $mAcm^{-2}$) without the need for using metallic current conducting components, normally nickel and without significant carbon formation and deposition when using hydrocarbon fuels. Unlike previously tried doped $LaCrO_3$ in which a small number of the La and/or Cr atoms in $LaCrO_3$, typically 5 to 10%, or at most 20 %, are replaced by different atoms, resulting in a doped form of a "single" perovskite, in a double perovskite material the B sites of the perovskite crystal lattice structure, normally occupied substantially wholly by Cr, is occupied by similar amounts of two different elements.

Thus in one aspect the present invention provides a novel material suitable for use in an anode in a solid oxide fuel cell, wherein the material is of an, optionally doped, double perovskite oxide material having the general formula I:

$$(Ln_aX_b)_e(Z^1{}_cZ^2{}_d)O_3 \quad (I)$$

wherein Ln is selected from Y, La and a Lanthanide series element, or a combination of these and X represents an optional second element occupying the A site of a perovskite oxide and is selected from Sr, Ca and Ba, and Z^1 and Z^2 represent different elements occupying the B site of a perovskite oxide and are selected from Cr, Mn and Fe, and wherein a has a value from 0.7 to 1.0, b has a value of from 0.3 to 0, and each of c and d has a value of from 0.25 to 0.75, provided that a + b has a value of 1, and c + d, has a value of not less than 0.8, and wherein e has a value of from 0.8 to 1.

Thus it will be appreciated that although the Z^1 and Z^2, elements are preferably present in substantially equivalent

amounts, they can nevertheless depart to some extent from exactly equivalent amounts. Also it is possible for the A site in the perovskite material (occupied by X^1 and X^2), to be somewhat depleted without disrupting the crystal structure thereof and significantly degrading the properties of the anode.

The novel double perovskite materials provided by the present invention can be used in the production of anodes for use in SOFCs and which have significantly improved electrochemical performance, electrical and catalytic properties when compared with anodes of previously known materials, when used with methane fuel, whilst avoiding the particular problems and disadvantages of previously proposed electrodes such as Ni-YSZ. More particularly it has been found that they are chemically redox stable, which may significantly decrease the volume instability during redox cycling that causes degradation.

Preferably Z^1 and Z^2 represent Cr and Mn, respectively. Advantageously X represents Sr.

Although it is a particular feature of the electrodes provided by the present invention, that they have a distinctly different nature and composition from the previously known doped single perovskite materials, the double perovskite materials used in accordance with the present invention may nevertheless also be doped to some extent i.e. any one or more of the A and B sites which would otherwise be occupied by Ln, X, Z^1 and Z^2, may be replaced to a limited degree by one or more suitable dopant elements in order to improve still further electrical and/or catalytic properties.

Suitable dopants at the B sites i.e. replacing either or both of some Z^1 and some Z^2 sites, for improving electrical conductivity include V, Fe, Cu, Co and Ni, whilst suitable dopants for improving catalytic activity include Pd, Ce, Ni, Ru and Mg. In general the dopant should not occupy more than

more compounds consisting essentially of the required metallic elements in suitable proportions, in the form of suitable oxides or salts with nitric acids, are brought together into intimate admixture with heat treatment. One convenient method comprises a solid state reaction in which dry oxides and/or carbonates (or other salts such as acetates, oxalates etc) of the metal elements are mixed together and fired at a high temperature, typically of the order of 1000 to 1400°C. Another convenient method comprises combustion synthesis in which a solution of salts such as nitrates of the required metal elements in suitable proportions, in aqueous ethylene glycol, from which solution water is progressively removed to yield a gel which can be burnt to provide a char. Firing of the char at high temperature, typically above 1100°C, then yields the double-perovskite form of the material.

In order to make the material suitable for use as a fuel cell electrode, it is necessary for it to be in a relatively porous form which presents a relatively large surface area for chemical interactions to take place at. Preferably the electrode should have a porosity value of at least 20%, typically around 50%. In general suitably porous forms of the novel double perovskite material may be obtained by the addition of pore-forming agents (PFAs). The PFAs could be one or more of carbon and organic materials, such as PVB (polyvinyl butyral), PEG, terpineol, ethyl cellulose etc.

The anodes of the present invention may be used in various forms and configurations of SOFCs. Thus they may be used as anode or cathode in planar or tubular SOFC or SOFC rolls.

The anodes of the invention are substantially compatible with various electrolytes used in SOFCs, including in particular doped ceria and especially perovskites such as Sr- and Mg-doped LaGaO3 etc.

In a further aspect the present invention provides a SOFC having an anode according to the present invention.

It is also possible in at least some cases to use the new double perovskite materials provided by the present invention, in fuel cell cathodes, and accordingly the present invention also extends to a fuel cell cathode comprising a substantially porous body of a double perovskite according to the present invention. This provides the opportunity to use the same material as both cathode and anode in a SOFC with clear advantages with regard to compatability issues.

Further preferred features and advantages of the invention will appear from the following detailed examples given by way of illustration, and drawings in which:
Figs. 1, 3 and 4 are graphs showing measurement of various electrical properties obtained using anodes of the invention; and
Fig. 2 is a schematic drawing of the principal parts of an electrochemical cell of the invention in sectional elevation; and
Fig. 2A is an underside plan view of the cell of Fig.2.

Example 1 - Preparation of Double Perovskite Material

La_2O_3 (4.8873g), $SrCo_3$ (1.4763g), Cr_2O_3 (1.5199g) and MnO_2 (1.7388g) in powder form were mixed together in an agate mortar. The mixed powders were transferred into a zirconia container, with addition some acetone or ethanol and ball-milled for 15 minutes twice, and then left for 10 hours in a fume cupboard to evaporate the organic component.

The dried powers were then subjected to a series of high temperature firing and intermediate grinding cycles using a muffle furnace, as follows:

1. 12 hours at 1400°C
2. 20 mins grinding
3. 12 hours at 1400°C

The above procedure yielded 9g of a double perovskite in the form of a powder having the composition $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$.

This phase exhibits a rhombohedral unit cell, a = 5.4562(3)Å, $\alpha = 60.440\ (9)^\circ$.

Example 2 - Preparation of Double Perovskite Material

La_2O_3 (4.8873g), $SrCO_3$ (1.4763g) and $MnCO_3$ (2.299g) were dissolved in dilute nitric acid (40 mls 4 N) and heated to 80°C with stirring until a solution is obtained. Then 8.0028g $Cr(NO_3)_3 \cdot 9H_2O$ was dissolved into the solution. 25ml pure ethyl glycol was then added into the mixed nitrate solution and stirred at 80°C for 2 hours. The obtained gel was transferred into a porcelain container and heated on a hot plate until firing into char. The char was further heated at 1100 to 1400°C to obtain the perovskite oxide having the composition $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$.

Example 3 - Manufacture of Anode

The double perovskite material of Example 1 (0.45g) was mixed with 0.05g carbon (graphite) and 5ml ethanol. The mixture was ground in an agate mortar or ball-milled for 30 minutes to form a slurry. The slurry was painted or screen-printed onto an 8mol%Y_2O_3 stabilised zirconia 2 cm diameter disc with 2 mm thickness. The anode was then fired from room temperature heating up at 5°C/min up to 1100°C, held at 1100°C for 4 hours, and then cooled down to room temperature at 5°C/min. The thickness of the anode so obtained is about 30-100μm with an area of 1cm². A small amount of gold paste was partially coated onto the anode (ca. 50% coverage) and fired at 900°C for 30 minutes using a 5°C/min heating up and cooling down rate in the range from 300°C to 900°C, to ensure better electronic contact. Platinum paste (Engelhard Clal 6082) was painted onto the opposite side of the YSZ pellet and fired at 900°C for 30 minutes with 5°C/min heating up and cooling down rates above 300°C to provide a counter electrode (or cathode) and reference electrode.

Example 4 - Use of Anode

The anode obtained in Example 3 was mounted in a solid oxide fuel cell configured in the form of a 0.2mm thick layer of

YSZ electrolyte. $La_{0.8}Sr_{0.2}MnO_3$ (LSM) was coated onto the other side of the YSZ sheet to provide a cathode. The slurry composition used in the production of the cathode was 0.45g $La_{0.8}Sr_{0.2}MnO_3$, 0.05g graphite and 5ml ethanol. A thin layer platinum paste (see Example 3) was coated onto the LSM and fired at 900°C for 30 minutes with 5°C/min heating up and cooling down rates above 300°C to provide a cathode current collector.

Figure 1 shows the performance of the cell using the double perovskite oxide $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ anode of Example 3, when supplied with various different fuels: wet H_2, wet 5%H_2 or wet and pure CH_4, at 900°C. While the open circuit voltages (OCVs) for wet 5%H_2 and wet H_2 were close to the value predicted by the Nerst equation, 0.95 and 1.09V at 900°C, the OCV for wet and cyclinder CH_4 was 0.87 and 086V respectively, which is slightly lower than that for wet 5%H_2. The maximum power densities were higher for wet H_2 than wet 5%H_2, with values of 0.34W cm^{-2} and 0.17W cm^{-2} respectively. The maximum power density for wet methane was about 0.1W cm^{-2} at 0.53V, which is slightly lower than that for wet 5%H_2.

Example 5 - Properties of Anode

The properties of the anode of Example 3 were examined by means of a three-electrode configuration test cell illustrated schematically in Figs. 2 and 2A, which show a disc shaped electrolyte 1 with an annular anode 2 on one face 3 and an annular cathode 4 and a central disc-form reference electrode 5 on the opposite face 6. The electrolyte was sintered 8mol%Y_2O_3 stabilized ZrO_2 (YSZ) pellet with 2mm thickness and 20mm diameter. An anode with a thickness of about 50μm was deposited onto the YSZ electrolyte using an ethanol-based slurry and firing typically at 1000 to 1300°C. Pt paste (as previously described) was painted onto the other side of YSZ as counter or cathode, and reference electrodes. The anode over-potential with wet H_2 is shown in Fig. 3. It was found that the anode resistance decreases under polarization which is closer to the real operation conditions than OCV. The polarization resistance is less than $0.3\Omega/cm^2$

at a current density 300mA/cm^2. With further optimization, this performance could readily be improved even more. Fig. 3 shows the potential and current change at 925°C under operation using wet CH_4 as fuel at 0.4V bias. No significant performance degradation was observed during four hours operation although a trace amount of carbon was observed after the fuel cell performance in wet CH_4 and cooling down in the same atmosphere.

Example 6 - Preparation and use of Modified Anode

In some cells, a thin film interface of $Ce_{0.8}Gd_{0.2}O_2$ (CGO), prepared by a sol-gel process, was applied between the YSZ electrode and the anode, Anode polarisation resistance was further decreased with such a thin layer (5 μm)of CGO deposited between the YSZ electrolyte and LSCM anode as shown in Fig. 4. The polarization resistances in wet 5%H_2 and wet H_2 were about 0.62Ω cm^{-2} and 0.25Ω cm^{-2}, respectively. The anode polarization in wet H_2 at 925°C is comparable to that of the conventional Ni-YSZ cermet anode at 1000°C[10].

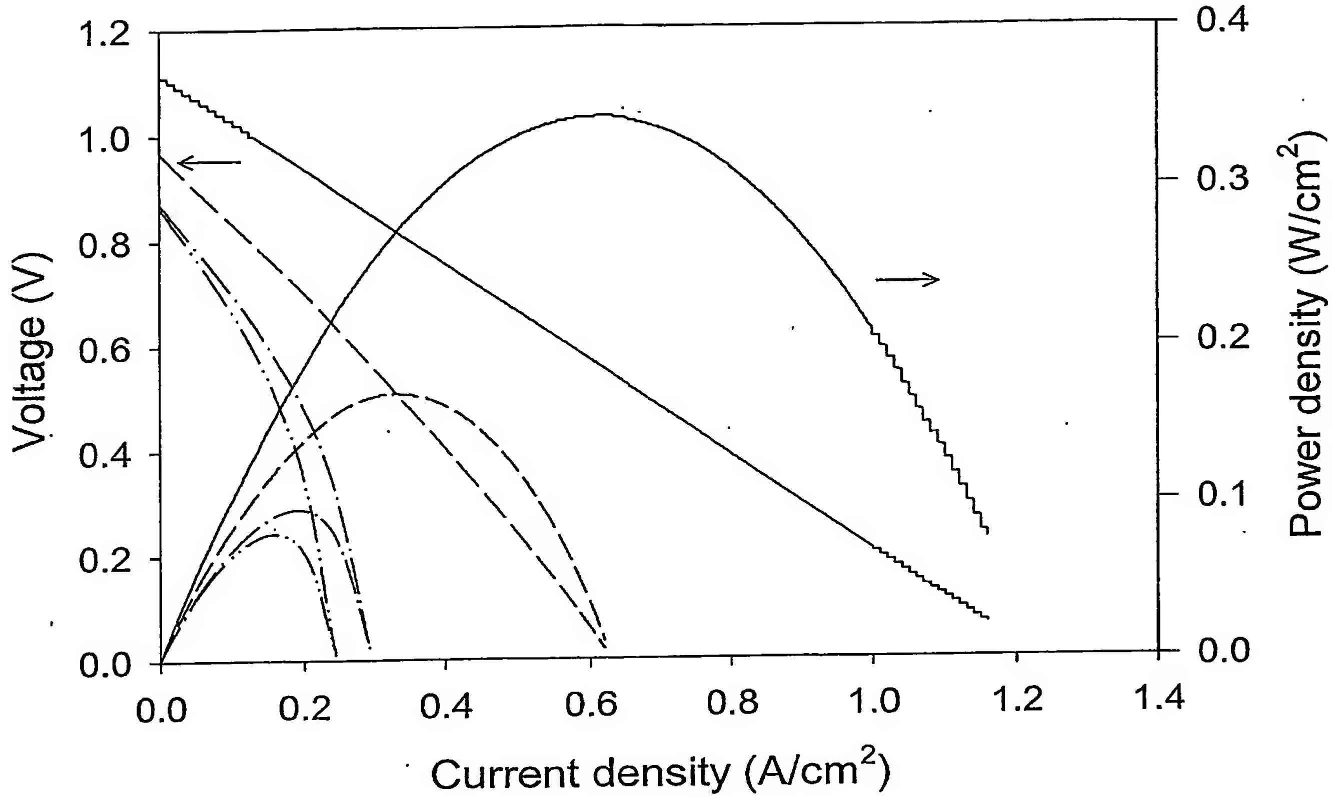

Figure 1 Power densities and current density-voltage relationships for an SOFC using the LSCM anode. The cell had a 0.2mm electrolyte, and data are shown for the following fuels: solid, wet H_2; dash, wet 5%H_2; dash-dot wet CH_4 and dash-dot-dot CH_4, at 1173K.

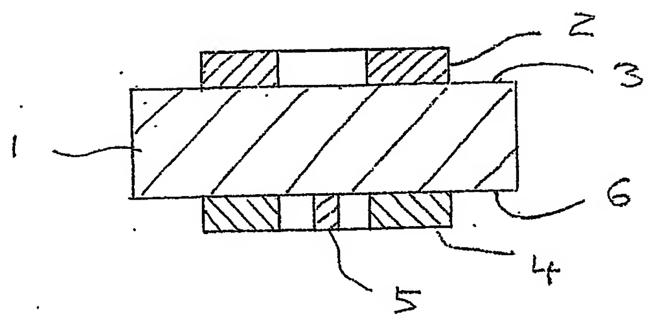

FIG. 2

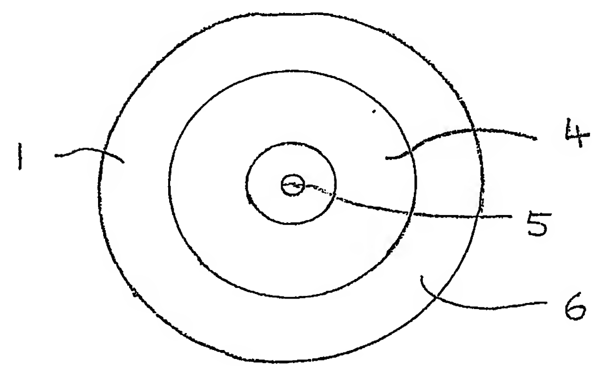

FIG. 2A

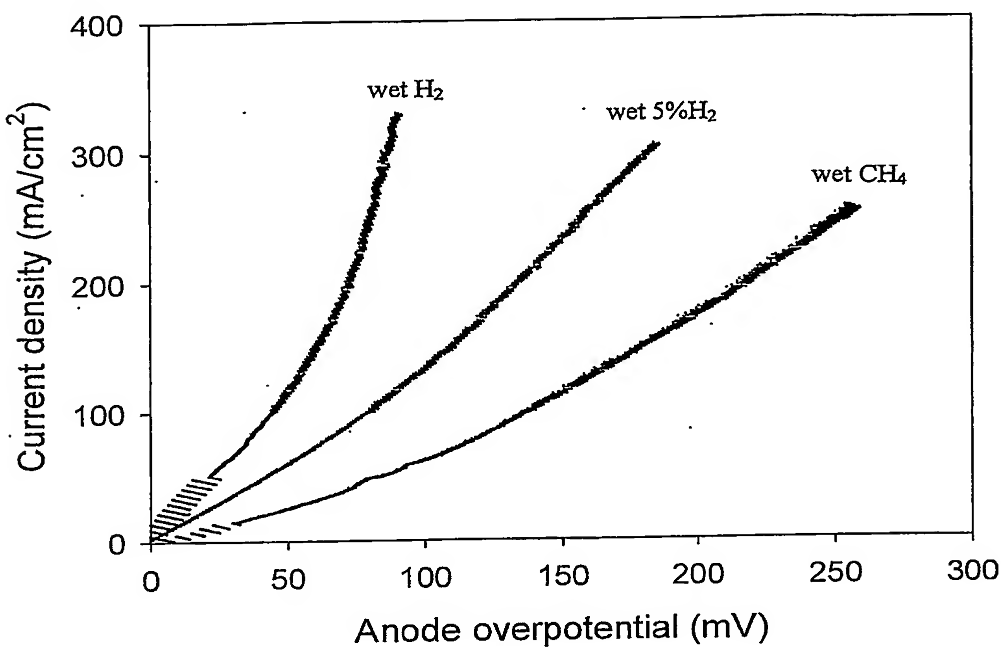

Figure 3 The anode overpotential at 925°C with different fuels using only $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ as anode

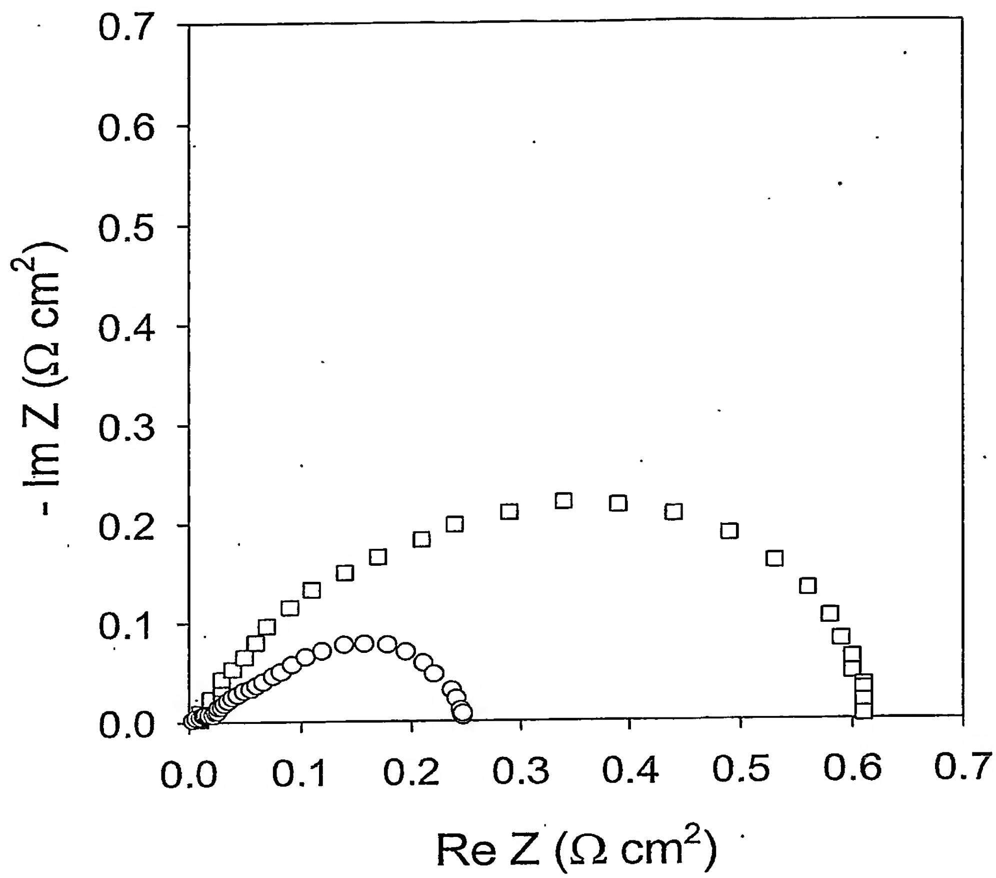

Figure 4 Comparison of electrode impedance spectra for LSCM/CGO anodes. Spectra were measured at 925°C in 4.9%H_2+2.3%H_2O+92.8%Ar (Y) and 97%H_2+3%H_2O (O). Three electrode configuration with LSCM/CGO as working electrode and Pt as counter and reference electrodes.